THE SYNTHESIS OF 3-*O*-[(BENZYLTHIO)CARBONYL]-β-D-GLUCOPYRANOSE AND METHYL 2,4,6-TRI-*O*-BENZOYL-α AND β-D-GLUCOPYRANOSIDES

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Received May 26, 1964

ABSTRACT

The discovery that the (benzylthio)carbonyl group is stable in concentrated hydrochloric acid has permitted the removal in that medium of isopropylidene blocking groups from 3-*O*-[(benzylthio)carbonyl]-1,2;5,6-di-*O*-isopropylidene-α-D-glucofuranose to furnish crystalline 3-*O*-[(benzylthio)carbonyl]-β-D-glucopyranose. Benzoylation of the latter provided a derivative which has made possible the synthesis of methyl 2,4,6-tri-*O*-benzoyl-α and β-D-glucopyranosides.

INTRODUCTION

Two of the four possible anomeric pairs of the tribenzoate derivatives of the methyl glucopyranosides have been known for many years. The use of the specific triphenylmethyl ether group to block the primary (C-6) hydroxyl group permits the syntheses of methyl 2,3,4-tri-*O*-benzoyl-α and β-D-glucopyranosides (1). The 2,3-di-*O*-benzoate of each methyl glucopyranoside, prepared with the aid of the 4,6-*O*-benzylidene blocking group, was specifically benzoylated at C-6 to furnish the 2,3,6-tri-*O*-benzoyl derivatives (2). A recent paper (3) described the synthesis of methyl 2-*O*-[(benzylthio)carbonyl]-α-D-glucopyranoside, which served as a precursor to methyl 3,4,6-tri-*O*-benzoyl-α-D-glucopyranoside, by a specific substitution of the (benzylthio)carbonyl group at C-2 in methyl 4,6-*O*-benzylidene-α-D-glucopyranoside. The thiocarbonate ester, $C_6H_5—CH_2—S—CO—O—$, serves as a useful blocking group for the synthesis of partial esters of carbohydrates due to the ease with which it can be removed without cleavage of other ester groupings (4).

Attempts to duplicate this specific substitution reaction at C-2 with methyl 4,6-*O*-benzylidene-β-D-glucopyranoside resulted in the recovery of disproportionately high yields of the disubstituted product. This method does not serve, therefore, as a practical route to methyl 3,4,6-tri-*O*-benzoyl-β-D-glucopyranoside.

The synthesis of 3-*O*-[(benzylthio)carbonyl]-1,2;5,6-di-*O*-isopropylidene-α-D-glucofuranose has been described (4). Attempts to remove selectively the isopropylidene groups from this compound by treatment with acid under refluxing conditions resulted also in the hydrolysis of the (benzylthio)carbonyl group. A method of removing the isopropylidene groups has now been found which provides crystalline 3-*O*-[(benzylthio)carbonyl]-β-D-glucopyranose and, ultimately, methyl 2,4,6-tri-*O*-benzoyl-α and β-D-glucopyranosides. Thus, all of the isomeric tribenzoate derivatives of methyl-α-D-glucopyranoside have now been characterized and, in the β-series, only the 3,4,6-isomer remains unknown.

RESULTS AND DISCUSSION

When methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (I) is treated with 1.1 moles of (benzylthio)carbonyl chloride (II) in pyridine solution, a 58% yield of the pure 2-*O*-

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[(benzylthio)carbonyl] derivative of I is obtained, together with 10% of the 2,3-di-*O*-[(benzylthio)carbonyl] derivative (3). Repeated attempts to duplicate this experiment using methyl 4,6-*O*-benzylidene-β-D-glucopyranoside (III) and 1 mole of II resulted in the recovery of 40% of the disubstituted derivative (IV), previously described (4). From the remaining products, consisting necessarily of 40% of unreacted III, a monosubstituted product could be isolated only in very low yield.

It can be calculated[3] from considerations of chemical kinetics that 33.3% of the disubstituted product would be formed if it is assumed that the hydroxyl groups have equal reactivities which are not changed after substitution at the other position (see appendix). Substitution of the (benzylthio)carbonyl group at one of the hydroxyl groups would be expected to activate the remaining hydroxyl group (5). This activation can account for the high proportion (40%) of disubstituted product formed when the substitution is carried out on the β-glucoside. One explanation for the low yield (10%) of disubstituted product in the case of substitution in the α-glucoside is that the reactivity at C-2 is considerably greater than that at C-3 and substitution at C-2 does not increase the reactivity at C-3 sufficiently to enable it to compete with the more reactive C-2. This explanation is consistent with the observation (3) that all of the monosubstituted product isolatable in the case of the α-glucoside is that substituted at C-2. The radical difference in behavior of the α- and β-methyl glucosides encountered in these experiments was not expected.

Because of the low yield of mono-(benzylthio)carbonyl derivatives of III obtained, the synthesis of methyl 3,4,6-tri-*O*-benzoyl-β-D-glucopyranoside by this route is not practical. Another possible route to this compound was discarded, since repeated attempts to saponify preferentially one of the (benzylthio)carbonyl groups from the disubstituted product IV under mild conditions again resulted in the recovery of proportionately high yields of disubstituted and unsubstituted products.

Diethylmercaptal derivatives can be prepared directly from 1,2-*O*-isopropylidene derivatives by treatment with a mixture of concentrated hydrochloric acid and ethyl mercaptan (6). The behavior of 3-*O*-[(benzylthio)carbonyl]-1,2;5,6-di-*O*-isopropylidene-α-D-glucofuranose (V) in concentrated hydrochloric acid therefore was investigated. The optical rotation of a solution of V in concentrated hydrochloric acid at room temperature increased slightly and essentially was constant after 20 h. Evaporation of the acid *in vacuo* yielded a crystalline reducing product (VI) which was homogeneous, and readily distinguishable from D-glucose, on paper chromatograms. The pure product showed a mutarotation of $-4.3° \rightarrow +60.2°$ (in acetone), indicative of a β-configuration. Its elemental analysis agreed with that calculated for a mono-(benzylthio)carbonyl derivative of glucose.

The crystalline (benzylthio)carbonyl-D-glucose derivative VI was shown to have the β-pyranose configuration by the sequence of reactions shown in Fig. 1. Benzoylation in pyridine gave a tetrabenzoyl derivative (VII). Levene and Meyer (7) found that β-D-glucopyranose, under similar conditions, yielded the pentabenzoate derivative without any accompanying change in the configuration of the ring. Oxidative removal of the (benzylthio)carbonyl group from VII, followed by benzoylation of the regenerated hydroxyl group, gave a product (IX) having a melting point and optical rotation identical with those reported (7) for 1,2,3,4,6-penta-*O*-benzoyl-β-D-glucopyranose. The higher-melting crystalline form of this compound reported by Ness, Fletcher, and Hudson (8) was not encountered in this work. Migration of the (benzylthio)carbonate ester grouping

[3]*The authors would like to acknowledge the assistance of Dr. D. Prevorsek and Dr. S. Winchester, Textile Research Institute, in performing these calculations.*

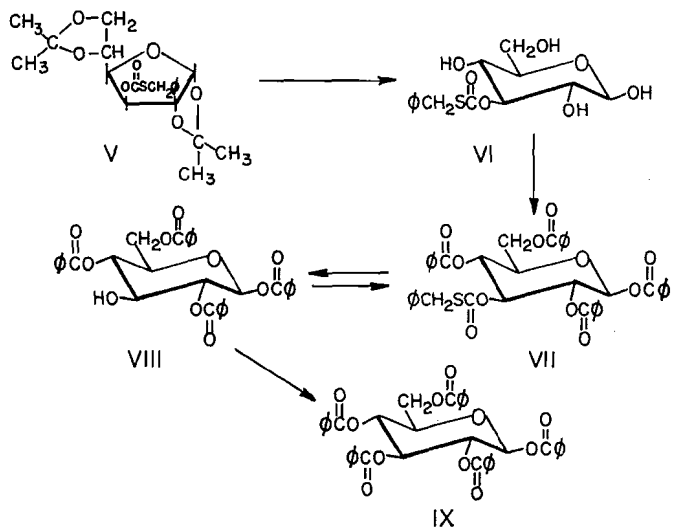

FIG. 1.

from C-3 under the acidic conditions used to remove the isopropylidene grouping is unlikely. The assignment of the (benzylthio)carbonate grouping to C-3 is confirmed by comparison of the physical properties of methyl 2,4,6-tri-*O*-benzoyl-α-D-glucopyranoside (XV) and its derivatives, subsequently synthesized, with those of the known 2,3,4-, 2,3,6-, and 3,4,6-derivatives.

When treated with (benzylthio)carbonyl chloride, VII was resynthesized from VIII, proving the absence of benzoyl migration during the removal of the (benzylthio)carbonyl group. The 3-*O*-acetyl and 3-*O*-(*p*-tolylsulphonyl) derivatives of VIII were prepared.

The 3-*O*-[(benzylthio)carbonyl]-tetra-*O*-benzoyl derivative (VII) was then used to synthesize methyl 2,4,6-tri-*O*-benzoyl-α and β-D-glucopyranosides, as shown in Fig. 2. Peracetylated hexoses are converted to the acetochlorohexose on treatment with titanium tetrachloride in chloroform (9). This method has been shown, more recently, to be applicable to perbenzoylated glucose derivatives (8, 10). The presence of the (benzylthio)-carbonyl group did not cause any anomalous behavior during the use of this reagent. The α-chloro derivative (X) was converted smoothly to methyl 2,4,6-tri-*O*-benzoyl-3-*O*-[(benzylthio)carbonyl]-β-D-glucopyranoside (XI) when treated with silver carbonate in boiling methanol. Oxidative removal of the (benzylthio)carbonyl group gave methyl 2,4,6-tri-*O*-benzoyl-β-D-glucopyranoside (XII), which on benzoylation gave the known (8, 11) methyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside. The 3-*O*-(*p*-tolylsulphonyl) (XIII) and 3-*O*-acetyl derivatives of XII also were synthesized.

Anomerization of the β-glycosidic group in XI by a standard procedure (9) gave a sirupy product (XIV). Oxidative removal of the (benzylthio)carbonyl group gave a crystalline product, methyl 2,4,6-tri-*O*-benzoyl-α-D-glucopyranoside (XV), which on benzoylation gave the known (1, 8) methyl 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranoside; its 3-*O*-(*p*-tolyl-sulphonyl) derivative (XVI) was prepared in the usual manner.

The structures of methyl 2,4,6-tri-*O*-benzoyl-α and β-D-glucopyranoside (XII and XV) were related unequivocally to that of 1,2,4,6-tetra-*O*-benzoyl-β-D-glucopyranose (VIII) by

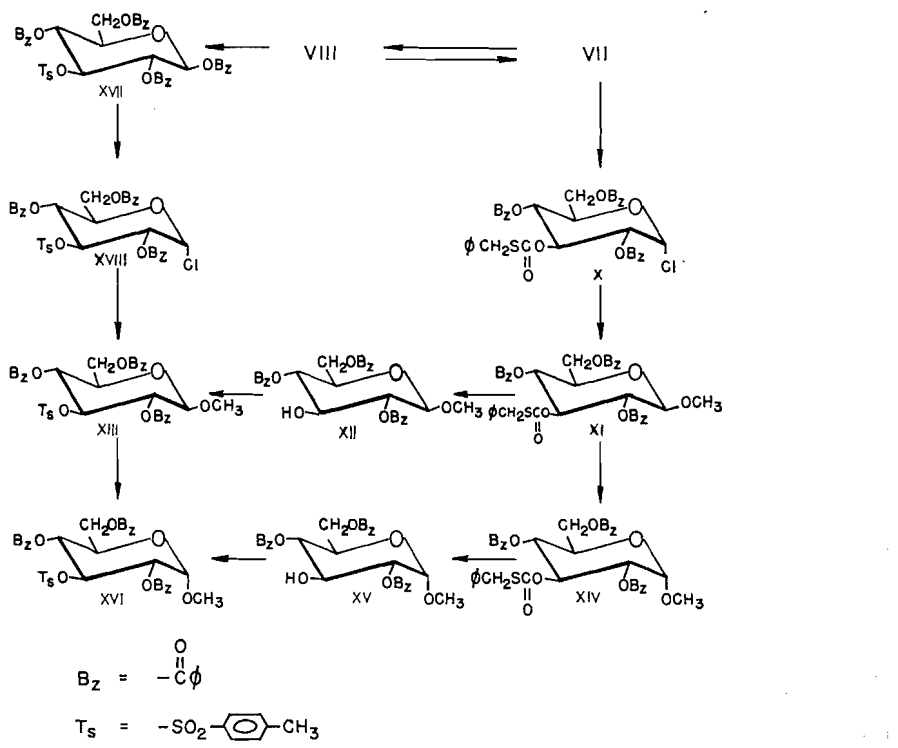

FIG. 2.

taking the *p*-tolylsulphonyl derivative (XVII) through the reaction sequence (XVII → XVIII → XIII → XVI) shown in Fig. 2. The *p*-tolylsulphonates (XIII and XVI) thus obtained were indistinguishable from those derivatives prepared from methyl 2,4,6-tri-*O*-benzoyl-α and β-D-glucopyranosides, respectively.

APPENDIX

The reaction of the methyl 4,6-*O*-benzylidene-α and β-D-glucopyranosides (I), containing two reactive hydroxyl groups, with 1 mole of (benzylthio)carbonyl chloride (II) falls into the class of competitive, consecutive (series) second-order reactions treated by Frost and Schwemer (11). The reactions are represented by:

$$A + B \xrightarrow{k_1} C,$$

and

$$A + C \xrightarrow{k_2} D,$$

where A, B, C, and D represent the molar concentrations of II, I, monosubstituted glucoside, and disubstituted glucoside, respectively. To apply the above reaction scheme, two assumptions must be made: (1) the two hydroxyl groups in the unsubstituted state have equal reactivities, and (2) substitution in one hydroxyl group produces the same change in reactivity as substitution in the other. The above authors solved the rate equations

[1] $$dA/dt = -k_1AB - k_2AC$$

[2] $$dB/dt = -k_1AB$$

[3] $$dC/dt = k_1AB - k_2AC$$

[4] $$dD/dt = k_2AC$$

for the case where initial concentrations were set at $A_0 = 2B_0$.

In the present study it was necessary to solve the above rate equations for the case where $A_0 = B_0$. From a material balance, summing eq. [1] $-$ 2 $\times$ eq. [2] $-$ eq. [3] and integrating gave

[5] $$A - 2B - C = A_0 - 2B_0.$$

Since $A_0 = B_0$,

[6] $$C = -2B + A + B_0,$$

and substituting in eq. [1],

[7] $$dA/dt = (2k_1 - k_2)AB - k_2A^2 - k_2AB_0.$$

If one chooses as dimensionless quantities:

[8] $$\alpha = A/A_0; \beta = B/B_0; \tau = B_0k_1t; \kappa = k_2/k_1,$$

then eqs. [2] and [7] can be solved to produce

[9] $$d\alpha/d\beta = (1 - 2\kappa) + \kappa(\alpha/\beta).$$

Integration of eq. [9] gives

[10] $$\alpha = \left(\frac{1 - 2\kappa}{1 - \kappa}\right)\beta + \left(\frac{1}{1 - \kappa}\right)\beta^\kappa - 1,$$

the constant of integration being determined at $\alpha = \beta = 1$.

Solutions of eq. [10] for β as a function of α at different κ values are shown plotted in Fig. 3. The case of particular interest in the present study is that in which the reactivities of the hydroxyl groups are not changed after substitution, that is, $k_1 = k_2$ or $\kappa = 1$. The solution was obtained for $\kappa = 0.99$, as an approximation for $\kappa = 1$ which is not readily solvable. At $\alpha = 0$, it is seen that $\beta = 0.333$; that is, at the end of the reaction one-third of the initial I remains unsubstituted. Another one-third of the initial I must therefore be disubstituted, since the unsubstituted and disubstituted products must be equal at the end of the reaction. By difference, the remaining one-third of the initial I would be present as monosubstituted product.

To obtain the 40% of disubstituted product in the present work with the β-glucoside, it can be calculated that $k_2 = 2.5k_1$. The 10% yield of disubstituted product obtained with the α-glucoside can be interpreted to mean that $k_1 = 13k_2$.

EXPERIMENTAL

3-O-[(Benzylthio)carbonyl]-β-D-glucopyranose (VI)

3-*O*-[(Benzylthio)carbonyl]-1,2;5,6-di-*O*-isopropylidene-α-D-glucofuranose (V) was synthesized as previously described (4). The pure form (recrystallized from ethanol–water) had m.p. 75–77° and $[\alpha]_D^{20}$ −24.6° (*c*,2, $CHCl_3$).

One gram of V was ground in a mortar and dissolved in 3 ml of concentrated (37%) hydrochloric acid. After standing at room temperature for 18 h, the solution was evaporated *in vacuo* with a bath temperature

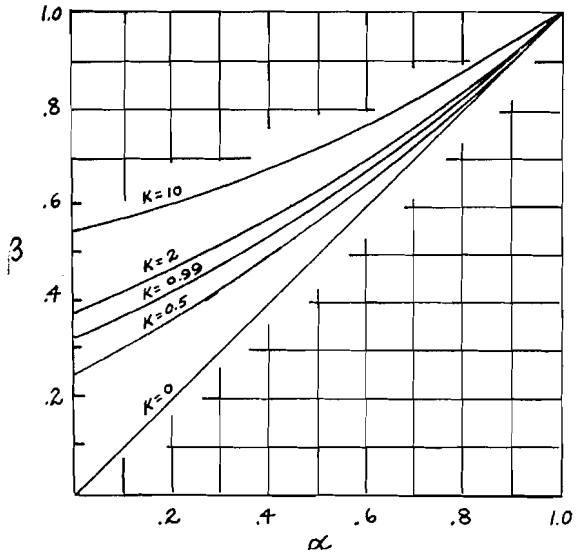

FIG. 3.

of 35–40°. The solid residue was washed with ice water until the washings were neutral and then dried *in vacuo* overnight over potassium hydroxide and phosphorus pentoxide. The product (0.78 g, 97%) reduced Fehling's solution and a paper chromatogram irrigated with butanol–ethanol–water (5:1:4, top layer) showed only one spot with R_f 0.87 (glucose R_f 0.17) when developed with alkaline silver nitrate. After recrystallization from boiling water, the product had m.p. 170–173° (decomp.), $[\alpha]_D^{21}$ −4.3° → +60.2° (*c*,1, acetone). The rotation reached a constant value after 26 h; it is seen that the acetone contained sufficient water to permit mutarotation.

Anal. Calcd. for $C_{14}H_{18}O_7S$: C, 50.91; H, 5.46; S, 9.70. Found: C, 50.64; H, 5.67; S, 9.59.

1,2,4,6-Tetra-O-benzoyl-3-O-[(benzylthio)carbonyl]-β-D-glucopyranose (VII)

To 2.0 g of VI in anhydrous pyridine (30 ml) was added benzoyl chloride (5.0 ml) with cooling in an ice bath. After standing overnight at room temperature, the solution was poured into ice water. The solid deposited was recovered by filtration and washed thoroughly with water. After drying, recrystallization from a mixture of acetone and ethanol gave the product (4.4 g, 98%) having m.p. 199–201°. Two further recrystallizations afforded the pure product having m.p. 200–202°, $[\alpha]_D^{24}$ −16.55° (*c*,1, $CHCl_3$).

Anal. Calcd. for $C_{42}H_{34}O_{11}S$: C, 67.57; H, 4.56; S, 4.28. Found: C, 67.46; H, 4.62; S, 4.11.

In a separate experiment, the solid product VI (50 g, m.p. 157–163°), obtained by evaporation of the hydrochloric acid but omitting the crystallization from water, was benzoylated in the same fashion and gave, after 1 crystallization, 100 g (89%) of VII, m.p. 190–194°. The pure product VII was obtained in 75% yield after 1 recrystallization.

1,2,4,6-Tetra-O-benzoyl-β-D-glucopyranose (VIII)

To a solution of VII (8.0 g) dissolved in chloroform (450 ml) and glacial acetic acid (550 ml) was added potassium acetate (2.0 g) and 30% hydrogen peroxide (150 ml). After standing for 7 days at room temperature, the solution was concentrated *in vacuo* (air-leak) to 150 ml, and water (30 ml) was added to turbidity. Cooling the mixture at 5° gave 6.3 g (98%) of product in 2 crops of crystals, m.p. 176–179°. Two recrystallizations from acetone–petroleum ether gave 5.6 g (89%) having m.p. 179–180° and $[\alpha]_D^{21}$ +8.7° (*c*,1, $CHCl_3$).

Anal. Calcd. for $C_{34}H_{28}O_{10}$: C, 68.46; H, 4.70. Found: C, 68.02; H, 4.82.

Derivatives of VIII

Derivatives of VIII were prepared from 0.5 g samples in pyridine solution by standard procedures. After 48 h reaction time at room temperature, each product was obtained as a solid by pouring the reaction mixture into ice water; filtration and recrystallization (twice) from acetone–petroleum ether afforded the pure compound.

1,2,3,4,6-Penta-O-benzoyl-β-D-glucopyranose (IX).—Yield: 0.45 g (77%); m.p. 156–158°; $[\alpha]_D^{19}$ +23.4° (*c*,1, $CHCl_3$). Reported (6): m.p. 157°; $[\alpha]_D$ +24° (*c*,3, $CHCl_3$).

3-O-Acetyl-1,2,4,6-tetra-O-benzoyl-β-D-glucopyranose.—Yield: 0.39 g (73%); m.p. 224–226°; $[\alpha]_D^{20}$ +9.4° (*c*,1, $CHCl_3$).

Anal. Calcd. for $C_{36}H_{30}O_{11}S$: C, 67.71; H, 4.70. Found: C, 67.39; H, 4.65.

1,2,4,6-Tetra-O-benzoyl-3-O-(p-tolysulphonyl)-β-D-glucopyranose (XVII).—Yield: 0.31 g (48%); m.p. 193° (decomp.); $[\alpha]_D^{20}$ +11.7° (*c*,1, $CHCl_3$). Another reaction using 4 days reaction time gave this product in 69% yield.

Anal. Calcd. for $C_{41}H_{34}O_{12}S$: C, 65.60; H, 4.54; S, 4.27. Found: C, 65.61; H, 4.59; S, 4.49.

2,4,6-Tri-O-benzoyl-3-O-[(benzylthio)carbonyl]-α-D-glucopyranosyl Chloride (X)

To a solution of VII (50 g) in pure, dry chloroform (1 500 ml) was added titanium tetrachloride (14.7 ml) and the solution was refluxed for 5 h with the exclusion of moisture. The product was isolated by pouring the solution on to ice pieces and by washing the separated chloroform layer with aqueous potassium bicarbonate and then 3 times with water. The dried ($MgSO_4$) chloroform solution was evaporated to dryness and the solid residue was recrystallized, first from acetone–ether and then from ethanol, to give the product (35 g, 78%), m.p. 139–141°. In purest form the product had m.p. 140.5–141° and $[\alpha]_D^{21}$ +122.8° (*c*,1, $CHCl_3$).

Anal. Calcd. for $C_{35}H_{29}O_9ClS$: C, 63.59; H, 4.39; Cl, 5.38; S, 4.84. Found: C, 63.33; H, 4.29; Cl, 6.14;[4] S, 4.97.

Methyl 2,4,6-Tri-O-benzoyl-3-O-[(benzylthio)carbonyl]-β-D-glucopyranoside (XI)

To a solution of X (6.3 g) in anhydrous methanol (600 ml) was added 15 g of freshly precipitated, dried silver carbonate and the mixture was refluxed (drying tube) for 5 h. The silver salts were removed by filtration of the reaction mixture prior to cooling. The product, which crystallized from the solution on addition of 50 ml of water, was dissolved in acetone and filtered through carbon to remove the last traces of silver salts. The acetone was evaporated and the residue recrystallized twice from ethanol to give the product (3.3 g, 53%), having m.p. 165–166° and $[\alpha]_D^{23}$ +24.9° (*c*,1, $CHCl_3$).

Anal. Calcd. for $C_{36}H_{32}O_{10}S$: C, 65.85; H, 4.88; S, 4.88. Found: C, 65.79; H, 5.08; S, 5.24.

Additional amounts of product could be obtained by further treatment with silver carbonate in methanol of the low-melting material obtained as final crops in the alcohol recrystallizations.

Methyl 2,4,6-Tri-O-benzoyl-β-D-glucopyranoside (XII)

The (benzylthio)carbonyl group was removed oxidatively from XI in the manner herein described for the synthesis of VIII. After 2 crystallizations from ethanol–water, the product (90%) had m.p. 152–154° and $[\alpha]_D^{21}$ +16.5° (*c*,1, $CHCl_3$).

Anal. Calcd. for $C_{28}H_{26}O_9$: C, 66.40; H, 5.14. Found: C, 66.16; H, 5.26.

Derivatives of XII

The following derivatives were prepared by standard procedures and were recrystallized twice from ethanol.

Methyl 3-O-Acetyl-2,4,6-tri-O-benzoyl-β-D-glucopyranoside.—Yield: 80%; m.p. 160–162°; $[\alpha]_D^{23}$ +28.4° (*c*,1, $CHCl_3$).

Anal. Calcd. for $C_{30}H_{28}O_{10}$: C, 65.69; H, 5.11. Found: C, 65.80; H, 5.26.

Methyl 2,4,6-Tri-O-benzoyl-3-O-(p-tolylsulphonyl)-β-D-glucopyranoside (XIII).—Yield: 78%; m.p. 191° (decomp.); $[\alpha]_D^{17}$ +33.9° (*c*,1, $CHCl_3$).

Anal. Calcd. for $C_{35}H_{32}O_{11}S$: C, 63.63; H, 4.85; S, 4.85. Found: C, 63.60; H, 4.94; S, 5.10.

Methyl 2,3,4,6-Tetra-O-benzoyl-β-D-glucopyranoside.—Yield: 66%; m.p. 158–160°; $[\alpha]_D^{19}$ +27.6° (*c*,1, $CHCl_3$). Reported (12): m.p. 160–162°; $[\alpha]_D$ +31° ($CHCl_3$).

Methyl 2,4,6-Tri-O-benzoyl-3-O-[(benzylthio)carbonyl]-α-D-glucopyranoside (XIV)

To a solution of XI (3.3 g) in pure, dry chloroform (300 ml) was added titanium tetrachloride (2.0 ml) and the solution was refluxed for 5 h. The product, isolated as described previously, could not be induced to crystallize and showed $[\alpha]_D^{21}$ +95.45° (*c*,2, $CHCl_3$).

Methyl 2,4,6-Tri-O-benzoyl-α-D-glucopyranoside (XV)

The product (XIV) from the foregoing experiment was treated in glacial acetic acid (100 ml) with potassium acetate (0.98 g) and 30% hydrogen peroxide (8.2 ml). The change in optical rotation was followed and attained a constant value after 9 days. The solution then was poured into 1 500 ml ice water and the solid product was recovered by filtration and was washed thoroughly. After drying, the product was crystallized twice from petroleum ether to give 1.82 g (72%), m.p. 74–76°, and $[\alpha]_D^{18}$ +94.9° (*c*,1, $CHCl_3$).

Anal. Calcd. for $C_{28}H_{26}O_9$: C, 66.40; H, 5.14. Found: C, 66.05; H, 5.02.

Derivatives of XV

Methyl 2,4,6-Tri-O-benzoyl-3-O-(p-tolylsulphonyl)-α-D-glucopyranoside (XVI).—This compound, prepared by the procedure previously described for XVII, had m.p. 163–165° and $[\alpha]_D^{18}$ +101.6° (*c*,0.8, $CHCl_3$).

[4]*The high value found in chlorine analysis can probably be attributed to interference from the sulphur present in the substance.*

Anal. Calcd. for $C_{35}H_{32}O_{11}$: C, 63.63; H, 4.85; S, 4.85. Found: C, 63.38; H, 4.75; S, 4.87.

Methyl 2,3,4,6-Tetra-O-benzoyl-α-D-glucopyranoside.—This compound, prepared as previously described, had m.p. 104–106° and $[\alpha]_D^{20}$ +84.2° (*c*,0.5, $CHCl_3$). Reported (7): m.p. 105–108° and $[\alpha]_D$ +84° (*c*,0.95, $CHCl_3$).

Synthesis of XIII and XVI from VIII. 2,4,6-Tri-O-benzoyl-3-O-(p-tolylsulphonyl)-α-D-glucopyranosyl Chloride (XVIII)

Compound XVII was treated in a manner identical with that for VII in the preparation of X. The product XVIII was crystallized twice from ethanol (yield 82%) and had m.p. 154–156°, $[\alpha]_D^{22}$ +123.8° (*c*,1, $CHCl_3$).

Anal. Calcd. for $C_{34}H_{29}O_{10}ClS$: C, 61.40; H, 4.36; Cl, 5.34; S, 4.82. Found: C, 61.45; H, 4.41; Cl, 6.36;[4] S, 5.04.

Compound XVIII was converted to XIII as described herein in the synthesis of XI from X. The product had m.p. 192° (decomp.) and $[\alpha]_D^{17}$ +32.8° (*c*,0.5, $CHCl_3$). A mixed melting point with XIII synthesized from XII was not depressed.

Anomerization of this product (XIII) to XVI, as described for the synthesis of XIV from XI, gave a product with m.p. 163–165° and $[\alpha]_D^{19}$ +102.4° (*c*,1, $CHCl_3$). Admixture with XVI, synthesized from XV, did not depress the melting point.

Resynthesis of VII from VIII

Compound VIII (0.15 g) was treated overnight in 2 ml pyridine with 0.15 g (benzylthio)carbonyl chloride and the solid obtained on pouring the reaction mixture into ice water was filtered off and recrystallized from acetone. The product (0.17 g), after 2 recrystallizations from ethanol, had m.p. 199–201° and did not depress the melting point of VII, obtained by benzoylation of VI.

ACKNOWLEDGMENTS

This investigation was carried out in part while one of us (J. J. W.) was supported by a Public Health Service Fellowship GPD-13,485-C1, from the Division of General Medical Sciences, Public Health Service. The same author would like to thank Professor M. Stacey for the use of his laboratories (1961–1963).

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